

On the kinetics and mechanism of dissolution of MgO crystals

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The kinetics of dissolution of $\{100\}$, $\{110\}$ and $\{111\}$ surfaces of MgO crystals have been investigated in H_2SO_4 and H_3PO_4 . It is observed that in concentrated H_2SO_4 and in concentrated and dilute H_3PO_4 , the etch rates change in the sequence $\{111\} > \{110\} > \{100\}$; and in dilute H_2SO_4 in the sequence $\{100\} > \{111\} > \{110\}$. From the etch rates determined for 4N H_2SO_4 , 36N H_2SO_4 and 4N H_2SO_4 –glycerine solutions at different temperature, the values of activation parameters are calculated. It is found that the value of the activation energy in a particular acid is practically constant for different planes, but that of the pre-exponential factor changes. Increase in the viscosity of 4N H_2SO_4 due to the addition of glycerine lowers the etch rate but the value of activation energy remains unchanged. However, in highly viscous 4N H_2SO_4 etchant, the value of the activation energy of selective etching decreases somewhat above $60^\circ C$, and the etch pits formed at dislocations are deeper and larger than those at screw dislocations. The results are discussed and the important conclusions are enumerated.

1. Introduction

Etching of $\{100\}$ faces of MgO crystals in aqueous acidic solutions is a common phenomenon and a number of acids and acidic salts form etch pits at the sites of dislocations [1, 2]. Studies on the kinetics of etching of $\{100\}$ faces of MgO showed [3, 4] that the process of dissolution is reaction-rate-controlled in HCl, HNO_3 , dilute H_2SO_4 and dilute H_3PO_4 , partly diffusion-controlled in concentrated H_3PO_4 and diffusion-controlled in concentrated H_2SO_4 . The diffusion-controlled nature of the process of dissolution was attributed to the high viscosity of the concentrated acid [3].

Although acids can be employed for the chemical polishing of a surface and selective etching of dislocations in MgO crystals, it is observed that the etching process depends on the crystallographic orientation of the crystal and on the nature of the acid [5]. Therefore, in order to understand the mechanism of etching it is worthwhile investigating the kinetics of etching of different faces and studying the effect of etchant viscosity on the activation parameters involved in the dissolution process of MgO crystals. The results of an investi-

gation dealing with these aspects are presented and discussed in this paper.

2. Experimental procedure

Specimens with $\{110\}$ and $\{111\}$ orientations were prepared by grinding on a Norton grinding wheel while those with $\{100\}$ planes were obtained by cleavage in the form of rectangular parallelepipeds having suitable dimensions (less than $10 \times 4 \times 4 \text{ mm}^3$) from a large MgO crystal obtained from Dr A. Briggs of AERE Harwell, UK. The $\{110\}$ and $\{111\}$ surfaces were polished in 44.1N H_3PO_4 at a temperature above $150^\circ C$ to remove the damaged layer caused by mechanical grinding. The rate of general polishing, v_p , was calculated from the initial and final dimensions, while the rate of dissolution, v_d , was computed from the loss in weight of the samples by dissolution after a suitable time. The lateral etch rate at dislocations, v_t , was calculated from the size of etch pits produced after a particular time. The method adopted to calculate v_d and v_t has been described earlier [3, 4, 6].

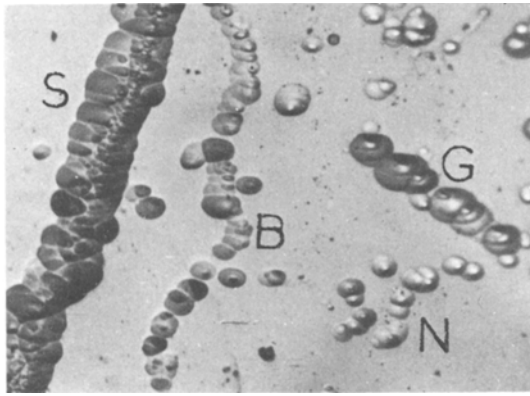


Figure 1 Etch pits formed on $\{110\}$ face by 4N H_2SO_4 at $54^\circ C$ after 30 min. Pits marked N and B and S and G correspond to old and fresh dislocations, respectively. $\times 150$

3. Experimental results

For etching studies we used 4N H_2SO_4 , 4N H_2SO_4 + glycerine (in different ratios), 36N H_2SO_4 , 2.21N H_3PO_4 and 44.1N H_3PO_4 solutions. Etchants based on H_2SO_4 were found to differentiate between fresh and old dislocations emerging on $\{100\}$ and $\{110\}$ surfaces; etch pits at fresh dislocations were deeper and larger than those at old dislocations. At $23^\circ C$, etch pits formed by 4N H_2SO_4 on the $\{100\}$ face were rounded squares with their sides parallel to $\langle 110 \rangle$ directions, whereas those on the $\{110\}$ face were elliptical with their major axis parallel to $\langle 110 \rangle$ directions. An example of etch pits produced on a $\{110\}$ face by 4N H_2SO_4 at $54^\circ C$ is illustrated in Fig. 1. Apart from the usual distribution of etch pits marked N, the figure also shows etch pits marked S around a scratch, B around a sub-boundary and G in a slip band. Etch pits formed

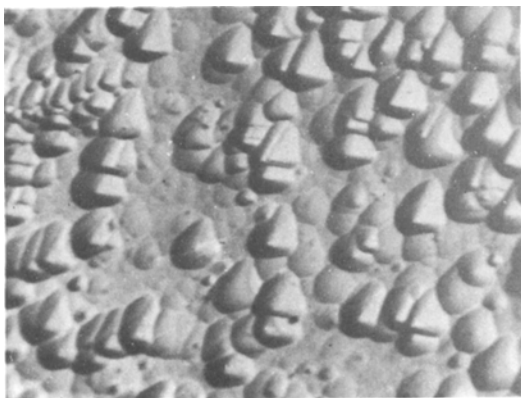


Figure 2 Etch pit pattern produced on $\{111\}$ face by 4N H_2SO_4 at $54^\circ C$ after 30 min. $\times 150$

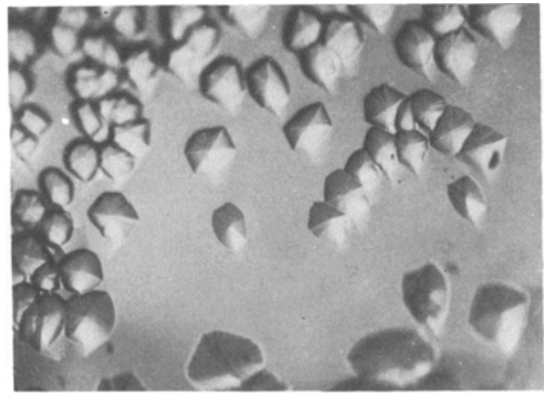


Figure 3 Overgrowths formed on a polished $\{110\}$ face by 36N H_2SO_4 at $31.5^\circ C$ after 30 min. $\times 150$

on $\{111\}$ faces (Fig. 2) were truncated triangles with their orientation similar to the outline of the face. However, it is not known whether the pits locate both old and fresh dislocations. In the case of 36N H_2SO_4 at $23^\circ C$, etch pits on the $\{100\}$ face were square with sides parallel to $\langle 100 \rangle$ directions, on the $\{110\}$ face they were rounded rectangles with longer sides parallel to $\langle 100 \rangle$ directions, and on the $\{111\}$ face they were rounded triangles with their orientation opposite to the outline of the face on which they were formed. In addition to etch pits, concentrated H_2SO_4 also formed hillocks on the $\{110\}$ (Fig. 3) and $\{111\}$ faces, similar to those observed previously on $\{100\}$ faces [1, 3].

Addition of glycerol to 4N H_2SO_4 did not produce hillocks as was anticipated from the increased viscosity of the etchant. Only dislocation etch pits

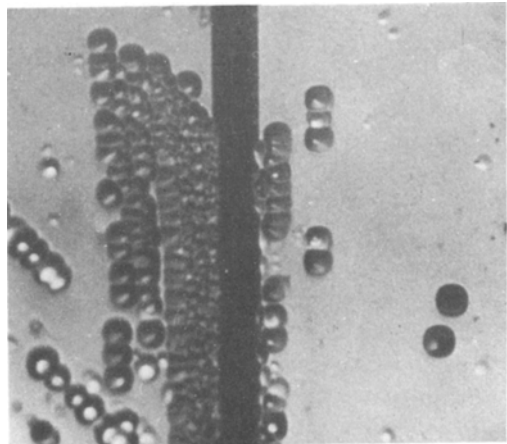


Figure 4 Example of etch pit pattern formed on $\{100\}$ face by an etchant composed from 8.6N H_2SO_4 and glycerol in the ratio (5:17). Etching time 1 h 35 min; temperature $23^\circ C$. $\times 200$

TABLE I Etching behaviour of H_3PO_4 on different planes of MgO crystals

Solution	Temperature (°C)	{100}	{110}	{111}
2.21N	23	Roughening with pits	Etch pits	Etch pits
	65	Roughening with pits	Etch pits	Etch pits
44.10N	23	Polishing with rare etch pyramids	Etch pits	Etch pits
	65	Polishing	Etch pits	Polishing
	110	Polishing	Etch pits	Polishing
	>150	Polishing	Polishing	Polishing

TABLE II Polishing rate, v_p ($cm\ h^{-1}$) in different solutions

Solution	Temperature (°C)	{100}	{110}	{111}
4N H_2SO_4	23	2.15×10^{-4}	1.65×10^{-4}	1.60×10^{-4}
36N H_2SO_4	23	1.00×10^{-4}	1.38×10^{-4}	1.38×10^{-4}
2.21N H_3PO_4	23	1.65×10^{-4}	1.50×10^{-4}	2.25×10^{-4}
	65	5.50×10^{-3}	3.75×10^{-3}	3.75×10^{-3}
44.10N H_3PO_4	65	5.30×10^{-3}	3.00×10^{-3}	3.95×10^{-3}

were formed and etching times were tremendously increased. The morphology of these etch pits was the same as of those produced by 4N H_2SO_4 solution, and they were also deeper and larger at fresh dislocations. Surprisingly, etch pits produced by 4N H_2SO_4 containing a high glycerine content were larger at edge dislocations than those formed at screw dislocations (Fig. 4). Measurements of the pit size on two different etched samples indicated that the etch pits formed at edge dislocations were about 20% larger than at screw dislocations. Therefore, while estimating selective etch rates on {100} faces, dimensions of pits formed only at screw dislocations were measured.

Concentrated H_3PO_4 acid at elevated temperatures polished {100} [1, 4] and {110} faces [1]. The results obtained by H_3PO_4 on {100}, {110} and {111} faces are given in Table I. Clearly 44.10N H_3PO_4 above 150°C polishes all three {100}, {110} and {111} faces of MgO crystals.

In the light of the results given in Table I 44.10N H_3PO_4 acid at a temperature above 150°C was used as a polishing agent whenever it was required to prepare {100}, {110} and {111} faces simultaneously for investigation. Solutions of 33.08N H_3PO_4 at 110 to 115°C and 44.10N H_3PO_4 at temperatures much below 150°C were also employed to polish the {100} face. Since at

higher temperatures polishing was fast, polishing times were suitably reduced.

The rate of polishing, v_p , of {100}, {110} and {111} planes of MgO crystals in H_2SO_4 and H_3PO_4 acid is given in Table II. From this table it is interesting to note that the values of v_p have the trend {100} > {111} \geq {110} for 4N H_2SO_4 , 2.21N H_3PO_4 and 44.10N H_3PO_4 solutions, while {111} = {110} > {100} for 36N H_2SO_4 .

The dependence of v_t on temperature in the interval between 20 and 75°C in the form of Arrhenius plots is shown in Figs. 5 and 6 for 4N H_2SO_4 and 36N H_2SO_4 respectively. The v_d and v_t versus $1/T$ plots for 4N H_2SO_4 -glycerol solutions are illustrated in Figs. 7 and 8. The estimated values of the activation energy, E_t , and the pre-exponential factor, A_t , for lateral etching at dislocations in 4N and 36N H_2SO_4 corresponding to {100}, {110} and {111} planes are given in Table III. The values of activation parameters for 4N H_2SO_4 -glycerine solutions are given in Table IV.

It may be noted from Table III that the values of E_t obtained for {100}, {110} and {111} planes in 4N H_2SO_4 and 36N H_2SO_4 are practically constant, whereas those of A_t change. In 4N H_2SO_4 , A_t decreases in the order {100} > {111} > {110}, whereas in 36N H_2SO_4 {111} > {110} > {100}. These orders also reflect the trends of the vari-

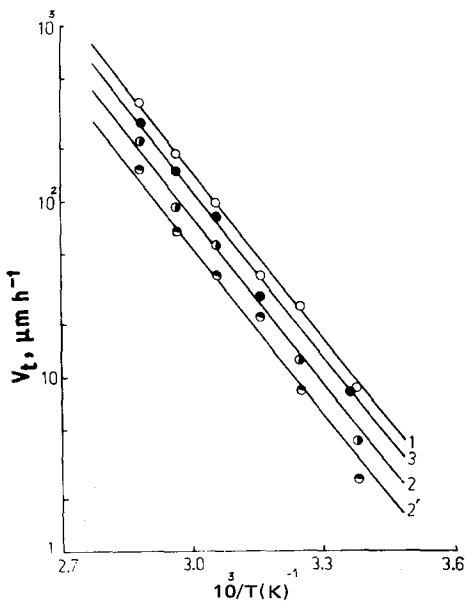


Figure 5 Plots of v_t versus $1/T$ for 4N H_2SO_4 . 1, $\{100\}$; 2, 2', $\{110\}$; 3, $\{111\}$. Curve 2 corresponds to pit dimension along semi-major axis, while curve 2' to that along semi-minor axis.

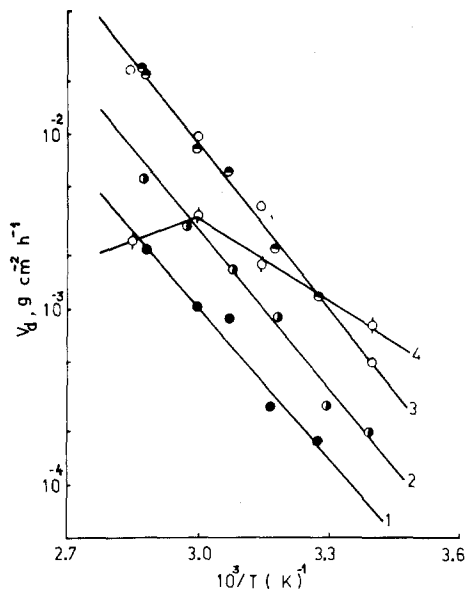


Figure 7 Plots of v_d versus $1/T$ for 4N H_2SO_4 + glycerine solutions. Ratios of 4N H_2SO_4 and glycerine: 1, (1:9); 2, (1:4); 3, (2:1). Curve 4 corresponds to data for 36N H_2SO_4 and the open circles on curve 3 are for 5.5N H_2SO_4 . Data for 36N H_2SO_4 and 5.5N H_2SO_4 are taken from [3]. Plane of observation $\{100\}$.

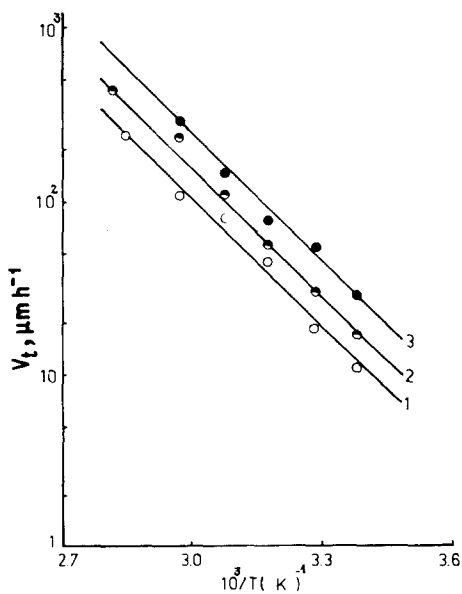


Figure 6 Plots of v_t versus $1/T$ for 36N H_2SO_4 . Curves 1, 2 and 3 correspond to the size of etch pit on $\{100\}$, $\{110\}$ and $\{111\}$ faces, respectively.

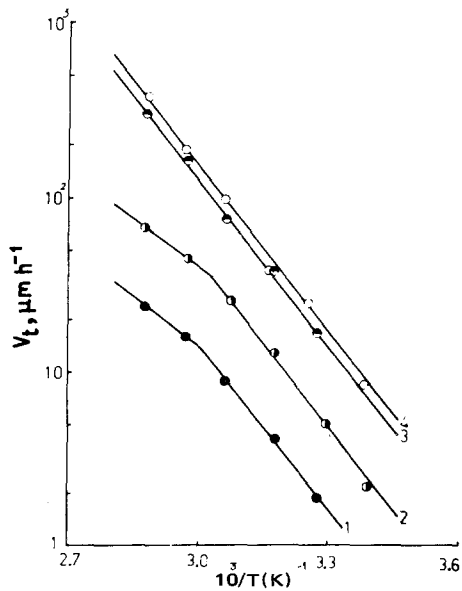


Figure 8 Graph of v_t versus $1/T$ for 4N H_2SO_4 + glycerol in different proportions. Ratios of 4N H_2SO_4 and glycerol: 1 (1:9); 2, (1:4); 3, (2:1); 4, (1:0).

TABLE III Estimated values of activation energy and pre-exponential factor for selective etching in H₂SO₄

Solution	{1 0 0}		{1 1 0}		{1 1 1}	
	E_t (eV)	A_t ($\mu\text{m h}^{-1}$)	E_t (eV)	A_t ($\mu\text{m h}^{-1}$)	E_t (eV)	A_t ($\mu\text{m h}^{-1}$)
4N H ₂ SO ₄	0.65	6.3×10^{11}	0.65	3.4×10^{11} * 2.4×10^{11}	0.65	4.7×10^{11}
36N H ₂ SO ₄	0.49	2.4×10^9	0.49	3.7×10^9	0.49	5.9×10^9

*Values corresponding to the dimensions measured along major and minor axes, respectively.

 TABLE IV Values of activation energy and pre-exponential factor of dissolution of the {1 0 0} face in 4N H₂SO₄ – glycerol solutions

4N H ₂ SO ₄ + glycerol,	E_t (eV)	A_t ($\mu\text{m h}^{-1}$)	E_d (eV)	A_d ($\text{g cm}^{-2} \text{h}^{-1}$)
1:0	0.65	6.3×10^{11}	–	–
2:1	0.65	5.1×10^{11}	0.62	2.4×10^7
1:4	0.65	1.9×10^{11}	0.60	3.9×10^6
1:9	0.65	6.1×10^{10}	0.57	5.9×10^5

ation of v_p in 4N and 36N H₂SO₄ for different planes (Table II).

It is also interesting to note from Table III that in the case of 36N H₂SO₄, the values of E_d and E_t are lowered but the difference $E_t - E_d$ is quite large as compared with that in 4N H₂SO₄.

From Figs. 7 and 8 and Table IV it may be seen that the obvious effect of the addition of glycerine to 4N H₂SO₄ is to lower the etch rates. When the amount of glycerine in 4N H₂SO₄ is less, E_t and E_d practically remain constant. However, for high glycerine contents, E_t decreases above about 60°C.

4. Discussion

Dissolution of a crystal involves (i) chemical reactions at the surface, and (ii) supply of the species being used in the reaction and removal of reaction product away from the surface. Since the transport mechanism of the supply of the reacting species to the surface and the removal of the reaction product is that of diffusion, the dissolution process can be diffusion-controlled or reaction-rate-controlled. Whether dissolution is diffusion-controlled or kinetically controlled can be decided by determining the activation energy for the process from the plot of log etch rate versus T^{-1} . Usually the value of the activation energy for a diffusion-controlled process is less than that for a kinetically controlled one [7]. If in an etchant different surfaces etch with practically the same rate, dissolution is believed to be diffusion-controlled [8].

4.1. Etch rate and activation energy

A high value of E_t for {110}, {110} and {111} faces in 4N H₂SO₄ (Table III) indicates that dissolution is chemically controlled irrespective of the plane under investigation. In the case of 36N H₂SO₄, in which dissolution is diffusion-controlled with a value of $E_d = 0.31$ eV, E_t is relatively high. This suggests that the dissolution processes at the surface and at dislocation sites are different. Different selective etch rates on different surfaces suggest that dissolution at dislocations is partly diffusion-controlled.

In 4N H₂SO₄–glycerol solutions, the values of E_d and E_t practically remain constant (Table IV) notwithstanding an increased viscosity of the etchant. This is contrary to expectation because, in principle, with increasing addition of glycerine, E_d should increase provided the dissolution process becomes diffusion controlled [3]. In particular, when the glycerine content in 4N H₂SO₄ is too high, the value of E_d should be equal to 0.67 eV, the activation energy of viscosity decrease (Fig. 9). In fact, from the constant value of E_d and a low value of E_t above a temperature of about 60°C it may be inferred that it is not just the viscosity of an etchant but other factors associated with the processes taking place at the surface and at dislocation sites, that govern the dissolution process.

Examination of Table V which includes the experimental rates of general polishing, v_p , and lateral etching, v_t , and the calculated rate of normal dissolution, v_n , at 23°C, shows that for different

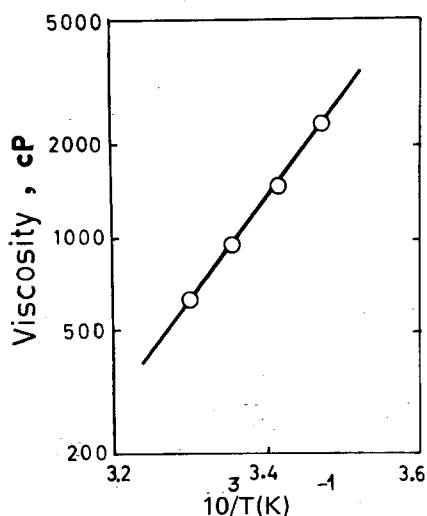


Figure 9 Graph showing the dependence of viscosity of glycerol on temperature.

planes the values of v_p are comparable with v_n in 4N H_2SO_4 . They are higher in 36N H_2SO_4 and the difference is quite marked for $\{110\}$ and $\{111\}$ planes. The order in which the rates of different planes change in the two etchants and the substantially higher values of calculated v_n as compared with v_p for 36N H_2SO_4 also indicate a difference in the nature of the dissolution processes in 4N H_2SO_4 and 36N H_2SO_4 .

Table VI compares the density of Mg atoms on different surfaces and that of free bonds at the surfaces and at dislocations. It shows that the number of free bonds at dislocations and the density of Mg atoms on different faces change in the sequence

$\{100\} > \{111\} > \{110\}$. Free-bond density, on the other hand, changes in the order $\{111\} > \{110\} > \{100\}$. These two sequences are observed to be followed in the dissolution of various faces in 4N H_2SO_4 and dilute and concentrated H_3PO_4 and in 36N H_2SO_4 , respectively. This implies that the number of free bonds at dislocations and the density of Mg atoms are the controlling factors when the dissolution process is partly or completely reaction-rate-controlled. In cases when the process is diffusion-controlled, surface free bonds govern dissolution.

It is easy to understand the role of the unsatisfied bonds at dislocations emerging on different surfaces in terms of the affinity with which the reaction species are attracted to them. However, the comparable values of v_p and v_n even when contrasting dislocation etch pits are present, must cast doubt on the role of dislocations.

Baranova and Nadgorny [9-12] have extensively studied the kinetics of etching and polishing of NaCl crystals in several solvents. According to them [10], v_p can be comparable with v_n when the rate of formation of dissolution centres and the movement of steps is the same for the free surface and the inclined faces of the pits; the process is possible even in the absence of dislocations because on the surfaces there are always major dissolution centres such as point defects, slip steps, crystal edges and so on. The nature of these centres, in turn, depends on the density of atoms on the surface.

To understand the nature of the processes in diffusion-controlled and kinetically controlled dis-

TABLE V Experimental rates of general polishing, v_p , and lateral etching, v_t , and calculated* rate of normal dissolution along dislocations, v_n , in $\mu m h^{-1}$ at 23° C in H_2SO_4

Etchant	$\{100\}$			$\{110\}$			$\{111\}$		
	v_p	v_t	v_n	v_p	v_t	v_n	v_p	v_t	v_n
4N H_2SO_4	2.15	8.65	1.75	1.65	4.40	0.88	1.60	7.00	1.40
36N H_2SO_4	1.00	9.30	1.86	1.38	15.30	3.06	1.38	29.3	5.86

*Taking $v_t/v_n = 5$.

TABLE VI Density of Mg atoms and free bonds at the surface and number of free bonds at dislocations on different MgO planes

Plane	Mg atoms cm^{-2}	Free bonds cm^{-2}	Number of free bonds at dislocations
$\{100\}$	1.1322×10^{15}	1.1322×10^{15}	2
$\{110\}$	0.8006×10^{15}	1.6012×10^{15}	1 $\{100\}$, 0 $\{110\}$ *
$\{111\}$	2.5148×10^{15}	2.5148×10^{15}	1 $\{100\}$, 2 $\{110\}$

* When the plane is missing to form an edge dislocation.

solution, consider the nature of the adsorption process in each case. In the case of kinetically controlled dissolution, where bonding of the atoms on the surface is not important, it can be assumed that physical adsorption involving weak forces of attraction between the crystal and the adsorbate takes place. In diffusion-controlled dissolution where the surface bonds are important, it is likely that chemical adsorption occurs.

4.2. Adsorption and the value of activation energy

Assuming that the dissolution of a crystal is a heterogeneous catalytic process, the entire process of chemical reaction at the crystal surface can be represented as one involving the following steps [13]:

- (1) adsorption of the reactants on the surface;
- (2) transfer of the adsorbed state into an active state;
- (3) reaction in the adsorbed state with the formation of adsorbed products;
- (4) desorption of the products.

If Q_a and Q_p are the heats of adsorption of the reactant and the reaction product and when the reactant is adsorbed weakly and the product strongly, the activation energy of a heterogeneous catalytic reaction may be represented by [13]:

$$E_{\text{cat}} = E - \Delta E - Q_a + Q_p. \quad (1)$$

Here E is the activation energy of the non-catalytic reaction and ΔE the enthalpy of adsorption of the activated complex on the catalyst (crystal). The values of the heat of adsorption, Q , appreciably depend on the fractional coverage of the surface and are usually unknown [13]. However, when multilayer adsorption predominates, the heat of adsorption is close to the heat of condensation, whereas below monolayer adsorption it has somewhat higher values [14]. The values of the heat of condensation of HCl, 100% HNO₃ and H₂O are 4.68, 9.09 and 11.00 kcal mol⁻¹, respectively [15]. The value of ΔE is low in physical adsorption and is < 9 kcal mol⁻¹ [16]. This corresponds to adsorption in the range of monolayer coverage.

The equations of the reaction rate are given by ([13], see also [3]):

$$v = \frac{Kc_a}{1 + K_a c_a}$$

and

$$v = \frac{Kc_a}{1 + K_p c_p}, \quad (2)$$

for moderate adsorption of the reactant and weak adsorption of the reaction product, and for weak adsorption of the reactant and moderate adsorption of the product, respectively. Here c_a is the acid concentration, c_p the product concentration, and K , K_a , K_p are constants. Both these expressions explain the nature of v versus c_a curves reported earlier [3]. Since the adsorption of the reaction product can be considered to be strong only at high acid concentrations, it follows from Equation 1 that in concentrated acid solutions, E_{cat} should be higher than that in dilute solutions. This is contrary to experimental results and hence it can be inferred that adsorption of the reaction product is weak in the dissolution of MgO. A similar conclusion was drawn earlier [17]. Equation 1 also indicates that the dissolution process involving physical adsorption of the activated complex is endowed with a high value of activation energy, while the one involving chemisorption has a low value of activation energy. From this it can be concluded that in order for the dissolution process to be diffusion-controlled, the system should have a high viscosity and involve chemical adsorption at the surface.

4.3. Effect of glycerine on dissolution

The effect of increased viscosity due to the addition of glycerine is to reduce the diffusion of the reacting and reacted species. Since the concentration of the reacting species at the surface is reduced by the increased viscosity of the etch, it is possible that the reaction rate is also reduced. This gives rise to a situation in which both diffusion and reaction rate are retarded, and the process of etching is still reaction-rate-controlled. A lowering in the value of E_t above 60° C in 4N H₂SO₄–glycerine in 1:4 and 1:9 volume ratios appears to be associated with the adsorption of glycerine molecules on the free bonds at the point of emergence of a dislocation.

It has been reported that aliphatic amines and acids assist the formation of dislocation etch pits on the B surfaces and of two types of etch pits corresponding to α and β dislocations on the A surfaces of III–V compounds [18]. Observations of the formation of etch pits with different characters at the sites of screw and edge dislocations

emerging on {100} faces of alkali halides are also known [19, 20]. In the present case, where the size of the etch pits at screw and edge dislocations and at fresh and old dislocations emerging on {100} and {110} faces of MgO is different, it appears that chemical factors are also important in the formation of etch pits.

5. Conclusions

(1) The number of free bonds at dislocations and the density of Mg atoms on the surface are the controlling factors when the dissolution process is partly or completely kinetically controlled. When the process is diffusion-controlled, the density of free bonds at the surface governs dissolution.

(2) The value of activation energy is high when the dissolution process involves physical adsorption. It is low when dissolution involves chemisorption.

(3) It was concluded [3] that the viscosity of the etchant determines whether or not the dissolution process is diffusion-controlled. Analysis of the results obtained in the present work shows that for a diffusion-controlled dissolution, the etchant should have a high viscosity and the system should involve chemisorption at the surface.

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